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⑤④ **Bleaching composition.**

⑤⑦ A bleaching composition is provided which comprises:

(A) hydrogen peroxide and or a hydrogen peroxide addition compound such as a percarbonate, perborate and perphosphoric acid;

(B) a hindered amine compound selected from the group consisting of heterocyclic hindered amines, acyclic hindered amine compounds and salts thereof; and

(C) an active halogen-containing compound capable of forming a hypohalogenous acid ion in an aqueous solution such as chloramine T and chloramine B. The bleaching composition may also contain a surfactant such as polyoxyethylene nonylphenyl ether in addition to the components (A) to (C) to improve the dirt-removing effect. By adding the specified hindered amine to the combination of the components (A) and (B), the synergistic effect thereof is further improved. Thus the composition exhibits an excellent bleaching effect at low temperatures without causing discoloration of colored cloths.

EP 0 315 204 A2

Bleaching Composition

BACKGROUND OF THE INVENTION

5 Field of the Invention

The present invention relates to a bleaching composition and a bleaching detergent composition which are suitable for bleaching fibers and clothes, particularly for washing and bleaching fibrous products.

10

Prior Art

Various compounds such as hypochloride, bleaching powder, hydrogen peroxide, hydrogen peroxide addition compounds such as sodium percarbonate, persulfates, isocyanurates, and organic peroxides have
15 been conventionally used as bleaching agents. Of these compounds, hydrogen peroxide and hydrogen peroxide addition compounds hardly affect the colors of colored and patterned clothes and are thus used as bleaching agents for clothes, namely they are widely used for bleaching out stains and black spots caused by tea, fruit juice, or cosmetics. However, such compounds have a problem in that their bleaching effects are generally low at low temperatures.

20 In order to solve the above-described problem, various different methods have been proposed in which various activators are added to bleaching agents to achieve effective bleaching at low temperatures.

Examples of such methods include a method in which a complex comprising EDTA and a heavy metal such as iron, manganese or cobalt is used as an activator to promote the decomposition of hydrogen peroxide (U.S. Patent No.315664) and a method in which a compound which produces peracetic acid when
25 reacted with hydrogen peroxide in a bleaching bath, i.e., carboxylic acid anhydride (U.S. Patent No.2362401) or an N-acylated compound (Japanese Patent Publication No.10165/1963) is used. However, the method using a heavy metal complex has a low activation efficiency and cannot provide a sufficient effect concerning bleaching at low temperatures. In addition, the method employing the addition of a peracetic acid-producing compound exhibits a high activation efficiency, but has disadvantages in that,
30 when stains such as tea or fruit juice stains are removed, the oxidative effect of the active oxygen species contained in the bath is too high and thus the dyes and coloring matters present on colored and patterned clothes are simultaneously oxidized, resulting in changes in color.

On the other hand, it is known that sodium N-chloro-p-toluene-sulphonamide, which is a N-halosulfonyl derivative, is used for the desizing and the bleaching purification of fibers (Japanese Patent Un-
35 Examined Publication No.110979/1969). In addition, a method has been proposed in which a halogen ion-producing compound such as a hypochlorite or a halogenated isocyanurate added to detergents is stabilized by using the above-mentioned sulfonyl derivative (Japanese Patent Un-Examined Publication No.14299/1986). However, even if these techniques are used, it is impossible to obtain a bleaching agent which exhibits an excellent effect of bleaching at low temperatures but which does not affect the colors of
40 colored and patterned clothes.

SUMMARY OF THE INVENTION

45 It is, therefore, a primary object of the present invention to provide a bleaching composition which exhibits an excellent effect concerning bleaching at low temperatures but which hardly affects the colors of colored and patterned clothes. This and other objects of the present invention will be clear from the following description.

Hydroxyl radicals ($\bullet\text{OH}$) and singlet oxygen ($^1\text{O}_2$) are known as active oxygen species which are
50 released from peroxide compounds and exhibit bleaching effects. The present inventors have found that, of these species, $\bullet\text{OH}$ has problems from the user's point of view in that it has a very high oxidative effect and exhibits a high bleaching effect on both the coloring matters of stains and also dyes, resulting in changes in the colors of colored and patterned clothes. On the other hand, it has also been found that $^1\text{O}_2$ exhibits a mild oxidative effect as compared with $\bullet\text{OH}$ and a low bleaching effect on dye coloring matters, but has a sufficiently high bleaching effect on the coloring matters as stains.

Various physical and chemical methods are known for the formation of singlet oxygen $^1\text{O}_2$ as described on page 198 of "Yuki Radical Oyobi Hikari Hanno (Organic Radicals and Photoreaction)" in "Yuki Kagaku Koza" 5 published by Maruzen Co., Ltd. on July 15, 1983. The inventors investigated the bleaching effect of a combination of H_2O_2 with a compound capable of forming a hypohalogenous acid ion in water from the points that they can be easily handled in water, have high safety and are inexpensive. Although the bleaching effect of the combination was higher than that obtained by using hydrogen peroxide alone, it was still practically insufficient in the points of the bleaching effect at low temperatures and changes in color of colored and patterned clothes.

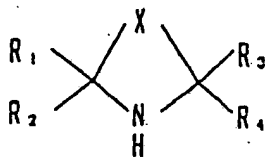
However, when a special hindered amine compound among amine compounds called "quenchers for $^1\text{O}_2$ " was added as the third component, surprisingly, the effects of the combination was further increased and a practically satisfactory bleaching level could be attained without discoloration.

The present invention provides a bleaching composition comprising:

- (A) hydrogen peroxide and/or a hydrogen peroxide addition compound,
- (B) a hindered amine compound selected from the group consisting of heterocyclic hindered amines, acyclic hindered amine compounds and salts thereof; and
- (C) an active halogen-containing compound capable of forming a hypohalogenous acid ion in an aqueous solution. The present invention provides also a bleaching detergent composition comprising the above-described components (A) to (C).

The component (A) used in the present invention is a compound which releases hydrogen peroxide in an aqueous solution. Examples of the hydrogen peroxide addition compounds include percarbonates, perborates, perphosphates and hydrogen peroxide addition compounds of urea. Examples of such salts include sodium salts, potassium salts, lithium salts, and calcium salts. Among these compounds, sodium percarbonate or sodium perborate or sodium perphosphates is preferably used.

The heterocyclic hindered amine compound (B-1) used as the component (B) in the present invention is preferably a compound having the following General Formula [I] or a salt thereof:



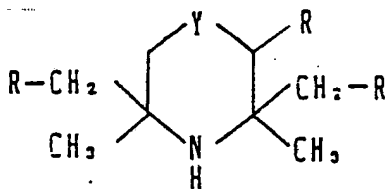
[I]

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(wherein R_1 to R_4 each donate a lower alkyl group and may be the same as or different from each other, or R_1 and R_2 or R_3 and R_4 may be bonded to each other to form a 5-membered or 6-membered alicyclic ring (i.e., cyclopentyl or cyclohexyl group) involving the carbon atoms to which they are bonded, and X donates a divalent organic residue).

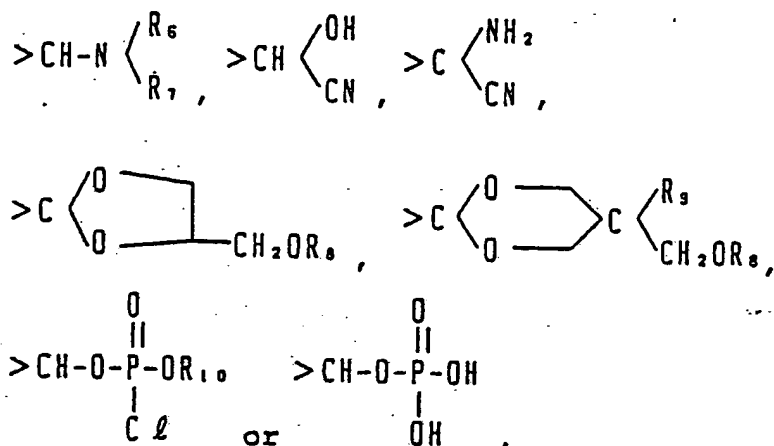
The lower alkyl groups include those having 1 to 4 carbon atoms, (i.e., methyl, ethyl, propyl, butyl or isobutyl group) preferably methyl group. Examples of the divalent organic residues include $-(\text{CH}_2)_4-$, $-\text{CH}_2\text{CH}_2-$, $-\text{CONH}-$, $-\text{CH}_2\text{CONHCH}_2-$ and $-\text{CH}_2-\text{Y}-\text{CH}_2-$. Y is the same as that in General Formula [II] which will be given below.

Among the compounds having the General Formula [I], those having the following General Formula [II] are particularly preferred:



[II]

(wherein R donates hydrogen atom or methyl group and Y donates $>\text{CH}_2$, $>\text{C}=\text{O}$, $>\text{CH}-\text{OR}_5$,

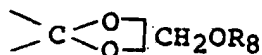


in which R_5 , R_6 , R_7 and R_8 may be the same or different and each donates a hydrogen atom, a lower alkyl group, $\text{C}_m\text{H}_{2m}\text{OH}$, $\text{C}_m\text{H}_{2m-1}(\text{OH})_2$, $\text{C}_m\text{H}_{2m}\text{COOM}_i$, m being an integer from 1 to 4 and M_i being a hydrogen atom or an alkali metal, an aliphatic, aromatic or araliphatic acyl group or a substituted or unsubstituted carbamoyl group; R_9 donates a methyl group or an ethyl group; and R_{10} donates a lower alkyl group or an aryl group).

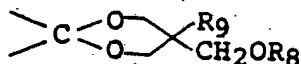
The alkali metals in the above-described formula include lithium, sodium and potassium. The aliphatic, aromatic and araliphatic acyl groups include a lower aliphatic acyl group (i.e., formyl, acetyl, propionyl, butyryl or isobutyryl), benzoyl, toluoyl and phenylacetyl groups. The substituted or unsubstituted carbamoyl groups include a carbamoyl group and a mono or di-lower alkyl carbamoyl group, preferably N-methylcarbamoyl group. The alkyl groups R_{10} include methyl and ethyl groups and the aryl groups R_{10} include phenyl and tolyl group. Preferred heterocyclic hindered amines of the present invention are those having formula [II] wherein R is hydrogen or methyl, Y is $>\text{CH}_2-$, $>\text{CH}-\text{OR}_5$ (in which R_5 is hydrogen or lower alkyl).



(in which both of R_6 and R_7 are hydrogen, or R_6 is hydrogen or lower alkyl and R_7 is lower aliphatic acyl, carbamoyl, mono or di-lower alkyl carbamoyl, or lower hydroxy-alkyl).



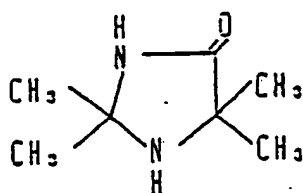
(in which R_8 is hydrogen, lower alkyl, lower aliphatic acyl, carbamoyl, or mono- or di-lower alkyl carbamoyl)
or



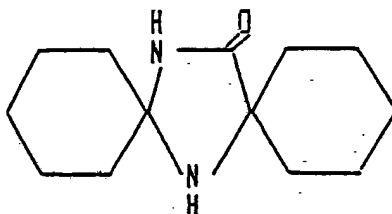
(in which R_8 is as defined above and R_9 is methyl or ethyl).

The amine compounds expressed by Formulae [I] and [II] are given in, for example, Japanese Patent Publication for Opposition Purpose (hereinafter referred to as "J.P. KOKOKU") Nos. 44-12414, 45-34815, 46-31733, 46-42618, 48-3211, 48-3212, 54-16980, 54-20977 and 59-20709. Examples are given below:

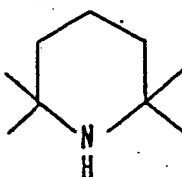
(1) 2,2,5,5-Tetramethyl-4-oxoimidazolidine:



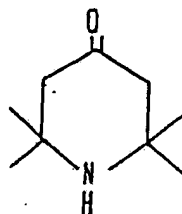
(2) 7,14-Diaza-dispiro[5.1.5.2]-pentadecane-15-on:



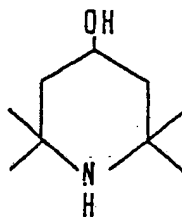
(3) 2,2,6,6-Tetramethylpiperidine:



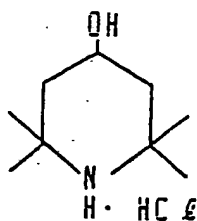
(4) 2,2,6,6-Tetramethyl-4-oxopiperidine:



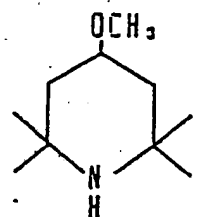
(5) 4-Hydroxy-2,2,6,6-tetramethylpiperidine:



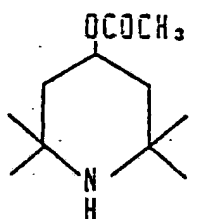
(6) 4-Hydroxy-2,2,6,6-tetramethylpiperidine hydrochloride:



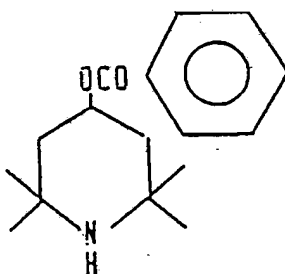
(7) 4-Methoxy-2,2,6,6-tetramethylpiperidine:



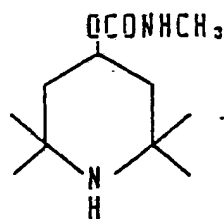
(8) 4-Acetoxy-2,2,6,6-tetramethylpiperidine:



(9) 4-Benzoyloxy-2,2,6,6-tetramethylpiperidine:

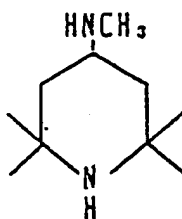


(10) 4-(Methylcarbamoyloxy)-2,2,6,6-tetramethylpiperidine:



(11) 4-Methylamino-2,2,6,6-tetramethylpiperidine:

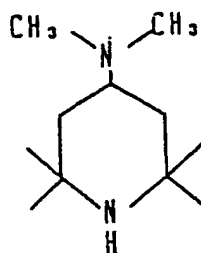
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(12) 4-(N,N-Dimethylamino)-2,2,6,6-tetramethylpiperidine:

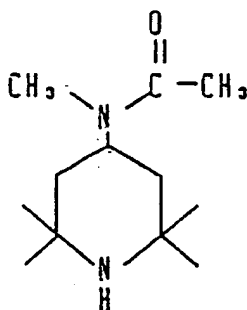
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(13) 4-(N-Acetyl)-N-methylamino-2,2,6,6-tetramethylpiperidine:

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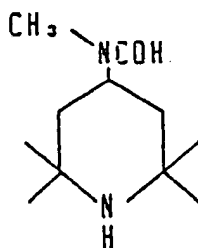


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(14) 4-(N-Formyl)-N-methylamino-2,2,6,6-tetramethylpiperidine:

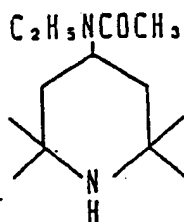
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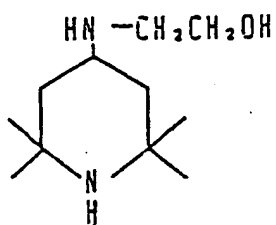
(15) 4-(N-Acetyl)-N-ethylamino-2,2,6,6-tetramethylpiperidine:

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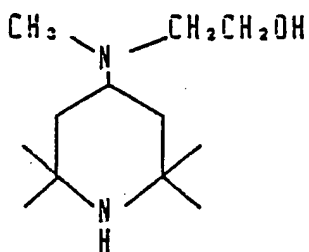


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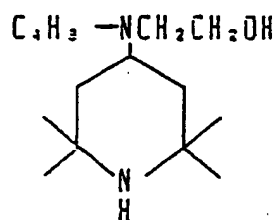
(16) 4-(2-Hydroxyethylamino)-2,2,6,6-tetramethylpiperidine:



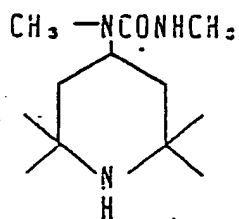
(17) 4-[N-(2-Hydroxyethyl)-N-methylamino]-2,2,6,6-tetramethylpiperidine:



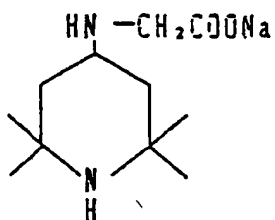
(18) 4-[N-(2-Hydroxyethyl)-N-butylamino]-2,2,6,6-tetramethylpiperidine:



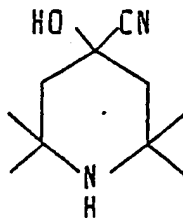
(19) 4-[N-(methylcarbamoyl)-N-methylamino]-2,2,6,6-tetramethylpiperidine:



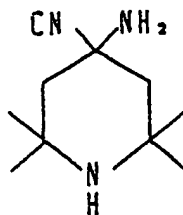
(20) Sodium N-(2,2,6,6-tetramethyl-4-piperidyl)glycinate:



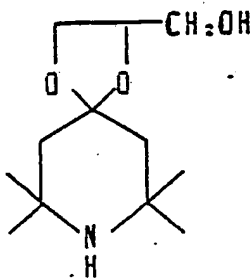
(21) 4-Cyano-4-hydroxy-2,2,6,6-tetramethylpiperidine:



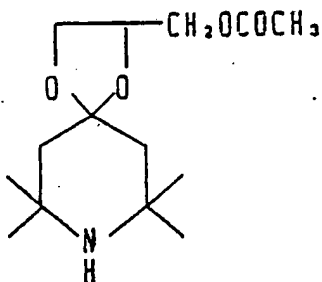
(22) 4-Amino-4-cyano-2,2,6,6-tetramethylpiperidine:



(23) 8-Aza-2-hydroxymethyl-7,7,9,9-tetramethyl-1,4-dioxaspiro-[4.5]decane:



(24) 8-Aza-2-(acetyloxymethyl)-7,7,9,9-tetramethyl-1,4-dioxaspiro-[4.5]decane:



(25) 9-Aza-3-ethyl-3-hydroxymethyl-8,8,10,10-tetramethyl-1,5-dioxaspiro[5.5]undecane:



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-COOR₅, in which R₅ is an alkyl group having 1 to 9 carbon atoms i.e., methyl, ethyl, propyl, butyl, isobutyl, pentyl, hexyl, heptyl, octyl or nonyl and, n is an integer of 1 to 9 and R₄ donates -H, -C_nH_{2n+1},

$-\text{C}(\text{C}_n\text{H}_{2n+1})_3$, $-\text{C}_n\text{H}_{2n}\text{OH}$,

$\text{CH}_2-\text{C}(\text{C}_n\text{H}_{2n+1})_3$,

$-\text{C}_n\text{H}_{2n-1}(\text{OH})_2$, $-(\text{C}_2\text{H}_4\text{O})_n\text{H}$,

$-\text{C}_n\text{H}_{2n}\text{COOH}$, $-\text{C}_n\text{H}_{2n}\text{COOR}_{16}$,

5 $-\text{C}_n\text{H}_{2n}\text{SO}_3\text{M}_2$, $-\text{C}_n\text{H}_{2n}\text{OSO}_3\text{M}_2$,

$-\text{C}_n\text{H}_{2n}\text{PO}_3\text{H}$ or $-\text{C}_n\text{H}_{2n}\text{CN}$,

in which R_{16} is an alkyl group having 1 to 9 carbon atoms defined above n is an integer of 1 to 9, and M_2 is H or an alkali metal defined above). Preferred acyclic hindered amines of the present invention are those

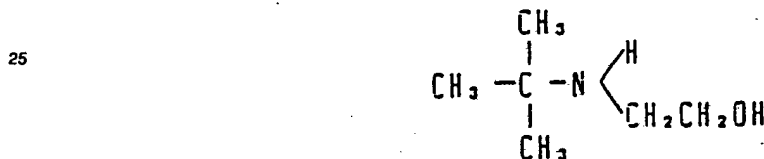
10 having formula [III] wherein each of R_{11} , R_{12} and R_{13} is $-\text{C}_n\text{H}_{2n+1}$ or $-\text{C}_n\text{H}_{2n}\text{OH}$ (in which n is 1 - 4) and R_{14} is H, $-\text{C}_n\text{H}_{2n+1}$, $-\text{C}_n\text{H}_{2n}\text{OH}$, $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$ or $-\text{C}_n\text{H}_{2n+1}\text{SO}_3\text{M}_2$ (in which n is 1 - 4 and M_2 is H or alkali metal).

Examples of the compounds of the above General Formula include:

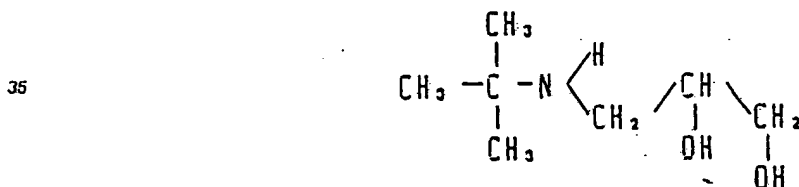
(28) t-Butylamine:



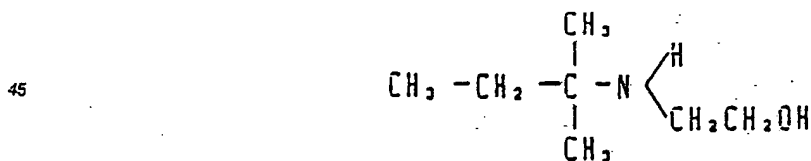
(29) 2-t-Butylaminoethanol:



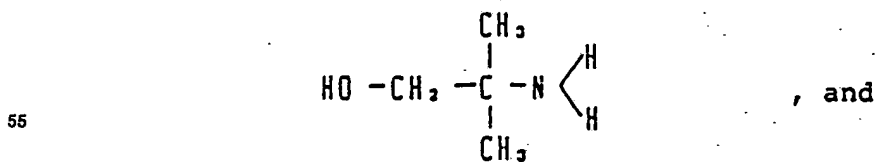
(30) 3-t-Butylamino-1,2-propanediol:



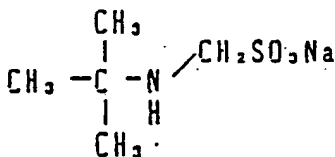
(31) 2-Dimethylpropylaminoethanol:



(32) 2-Amino-2-methylpropanol:



(33) Sodium t-butylaminomethanesulfonate:



These compound (B-1) can be used in combination with the compound (B-2).

These compounds (B-1) and (B-2) have a characteristic chemical structure in which a tertiary carbon atom is adjacent to an amino group.

Examples of the amine salts of the above General Formula [I] to [III] include salts of inorganic acids such as hydrochloric acid, sulfuric acid and phosphoric acid and organic acids such as acetic acid, propionic acid, benzoic acid and p-toluenesulfonic acid.

The component (C) used in the present invention may be any compound capable of forming a hypohalogenous acid ion upon dissolution in water to form ions or upon hydrolysis. The halogen of the hypohalogenous acid is preferably chlorine or bromine. The compounds as the component (C) include, for example, sodium N-chloro-p-toluenesulfonamide (chloramine T), sodium N-chlorobenzenesulfonamide (chloramine B), N-chlorosulfonamide, sodium N-cyclohexyl-N-chlorosulfonamide, N,N-dichlorosulfamoylbenzoic acid, N,N-dichloro-p-toluenesulfonamide (dichloramine T), N,N-dichlorobenzenesulfonamide, N-chlorosaccharin, N-chloromethanesulfonamide, N-chlorosulfamic acid, N-bromoacetamide, N-chlorosuccinimide, N-chlorohippurates, N-chloro-N-methylglycine, N-chloro-N-ethyl-o-carbobenzamide, N-chloroethylcarbamate, N-chloroacetanilide, N-chloro-o-carbobenzamide, N-chloro-N-methyl-o-carbobenzamide, chlorinated acetone/urea condensate, Na, Ca and Li hypochlorites, and mono- di- and trichloroisocyanuric acids. They can be used either singly or as a mixture of two or more of them. Among them, the N-halosulfonamides, N-haloamides, hypohalogenous acid salts and halogenated isocyanurates are preferred.

The present invention is characterized by using the above-described components (A), (B) and (C) in combination. By the synergistic effect of these three components, excellent bleaching power and prevention of changes in color can be achieved. Although the three components can be used in any ratio, it is preferred for obtaining an improved effect to use 0.05 to 4 mol, preferably 0.1 to 1.5 mol, of the component (B) and 0.05 to 4 mol, preferably 0.1 to 1.5 mol, of the component (C) per mol of hydrogen peroxide as the component (A) or hydrogen peroxide formed from the hydrogen peroxide addition compound.

~~The component (A) is used in an amount of 50 to 99% by weight (hereinafter referred to as "%"), preferably 60 to 95%; the component (B) is used in an amount of 0.5 to 40%, preferably 2.0 to 30%, and the component (C) is used in an amount of 0.5 to 40%, preferably 2.0 to 30%.~~

The components (A) to (C) used in the present invention can be granulated or surface-treated to control the dissolution velocity thereof depending on their use. An excellent effect can be obtained also when the component (A) is added after the addition of the components (B) and (C).

The bleaching composition of the present invention can be employed as it is or can be used as a bleaching agent in a mixture with conventionally-used components. In the latter case, the addition of 1 to 5% of a surfactant such as polyoxyethylene nonylphenyl ether (average oxyethylene chain length p = 5 to 30) can advantageously promote the permeation of bleaching components into clothes in water and improve the effect of stain removal.

~~In addition, the bleaching composition of the present invention can be added as a bleaching effect-imparting component to granular detergent. In other words, the bleaching composition can be desirably used as a bleaching detergent composition containing 0.1 to 30% by weight of the component (A), 0.1 to 30% by weight of the component (B), 0.1 to 30% by weight of the component (C) and 0.1 to 50% of at least one surfactant selected from the group comprising anionic surfactants, nonionic surfactants, and ampholytic surfactants, as well as conventionally-used components such as zeolite, an alkali builder, a perfume, and a dyestuff.~~

Furthermore, when the bleaching composition of the present invention is added to an enzyme-containing detergent, the effect concerning the removal of stains such as proteins is obtained by the enzyme effect acting on an article to be washed, whereby an excellent bleaching effect can be obtained. Since alkali protease, which is widely used in the industry related to this invention, is known to be inactivated by active chlorine, it is difficult to say that the activator used in the present invention is preferable for an enzyme if it is used singly. However, it was found that a system of the present invention in

which the activator composition of (B) and (C) is used in combination with hydrogen peroxide has only a slightly adverse influence upon an enzyme and shows an adequate bleaching effect.

Examples of the above-described anionic surfactants include linear alkylbenzenesulfonates in which the alkyl has 9 to 15 carbon atoms (C), alkylsulfates (particularly C₁₀ to C₂₂), olefin sulfonates (particularly C₁₀ to C₂₄), alkane and/or hydroxyalkane sulfonates (particularly C₁₀ to C₂₄), alkylphenoxy ether sulfates (particularly having C₈ to C₁₂ alkyl groups and 1 to 10 ethylene oxide units), alkyl ether sulfates (particularly, having C₁₀ to C₂₀ alkyl groups and 1 to 10, preferably, 2 to 4, ethylene oxide units), and mixtures of one or more kinds of soap (particularly C₁₂ to C₂₀).

Examples of the nonionic surfactants include the addition products of ethylene oxide or propylene oxide (typically 5 to 30 units) with aliphatic or aromatic alcohols or aliphatic amines or amides. Among these substances, aliphatic compounds preferably have C₈ to C₁₂ chains in the hydrophobic aliphatic portions thereof, and aromatic compounds preferably have alkyl aromatic groups having C₆ to C₁₂ chains.

Examples of the ampholytic surfactants include water-soluble derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium cationic compounds in each of which the aliphatic portion is a linear or branched chain, one substituent is C₈ to C₁₈, and an anionic water-soluble group, particularly a sulfonate group, is present at one end, such as alkyl hydroxypropanesulfonates and alkyl dimethylammonium-hydroxypropanesulfonates.

Examples of the detergent builders include sodium sulfate, sodium carbonate, sodium silicate, sodium pyrophosphate, sodium tripolyphosphate, nitrilotriacetic acid and water-soluble salts thereof, sodium ethylenediaminetetraacetate, and various aluminosilicates such as Zeolite A. In this connection, it is preferable that the bleaching-detergent composition contains a builder in an amount of 5 to 90% by weight.

Typical examples of enzymes include protease such as alkalase produced by Novo Corp., esperase, and sabinase and alkali cellulase. In this regard, the bleaching-detergent composition may contain an enzyme in an amount of 0.01 to 10% by weight.

~~The bleaching operation comprises dissolving or dispersing the composition in water and immersing textile fabrics in the solution. The amount of bleaching agent used can be suitably selected according to the desired degree of bleaching. In addition, a temperature within the range of 20 to 40°C is sufficient for bleaching, but one higher than 40°C may of course be employed.~~

The present invention can obtain an excellent bleaching effect at a relatively low temperature and is extremely suitable for domestic washing because it produces not discoloration of colored and patterned clothes, as experienced when conventional activators are used. In addition, since the present invention is not only free from any tendency to cause discoloration of colored and patterned clothes but is also capable of bleaching textile fibers or pulp fibers while at the same time reducing embrittlement, it is suitable for bleaching industrial threads and fabrics and for bleaching in paper-making processes.

The bleaching composition of the present invention is suitable also for the bleaching and deterging artificial teeth stained with sordes such as nicotine.

It is therefore obvious that the bleaching composition of the present invention can be widely used, and is also suitable for use as a bleaching agent for clothes. This bleaching composition is also useful as an additive for various detergents.

The present invention will now be described with reference to examples, though the present invention is not limited to these examples.

Examples

Description is now made of the method of forming stained cloth and dyed cloth and the method of measuring the bleaching effect and the degree of discoloration which were performed in Examples and Comparative Examples of the present invention.

Formation of stained cloth

Ten sheets of cotton broadcloth (pretreated cloth, 20 x 30 cm) scoured by desizing were placed in a solution of the dyestuff extracted from 20 g of black tea with 1 l of water which was boiled for 5 minutes and then dyed while being boiled for 30 minutes. Each stained cloth was wrung, dried with air, and then cut into pieces each having a size of 5 x 5 cm which were then used in bleaching tests.

Formation of dyed cloth

0.75 g of a dye (C.I.No. Reactive Red-21) and 13.5 g of anhydrous sodium sulfate were dissolved in 450 ml of water and three sheets of cotton broadcloth (20 x 30 cm) scoured by desizing were then placed in the obtained dye solution. The solution was maintained at 60° C for 20 minutes and 9 g of sodium carbonate was then added to the solution, which was then maintained at 60° C for 60 minutes. These sheets of cloth were then washed with water and then an aqueous 0.1% acetic acid solution, subjected to boiling treatment in an aqueous 0.2% anionic surfactant solution for 5 minutes, washed with water, dried, and then cut into pieces each having a size of 5 x 5 cm which were then used in discoloration tests.

Bleaching test

(i) Bleaching composition

Predetermined amounts of hydrogen peroxide or a hydrogen peroxide addition product and an activator were dissolved in 200 ml of water at 25° C. Five pieces of cloth stained with black tea were placed in this water bath and then subjected to bleaching treatment for 30 minutes. The cloths were then washed with water and dried to obtain bleached cloths. The degree of reflection of each of the pretreated cloth, black tea-stained cloth, and bleached cloth was measured by using a photoelectric reflection meter (ELREPHO produced by Carl Zeiss Co., Ltd.) and the bleaching ratio (%) thereof was obtained by the equation (3) described below.

(ii) Bleaching-detergent composition

A bleaching-detergent composition was added to water with a hardness of 3° DH at 25° C so that the concentration became 0.8%, and a cloth stained with black tea was immersed in the water bath in a bath ratio of 50 times and then allowed to stand for 30 minutes. A clean cotton knitted cloth and water with a hardness of 3° DH at 25° C were then added to the water bath and the bath ratio and the concentration of the detergent composition were adjusted to be 30 times and 0.15%, respectively, followed by washing with a Terg-O-Tometer (produced by U.S. Testing Co., Ltd.) for 10 minutes at 120 rpm. The pieces of test cloth treated in the above-described manner were dehydrated for 1 minute, rinsed with overflowing water for 1 minute, and dehydrated for 1 minute in turn with a washing machine, and then dried by ironing to obtain bleached cloths.

The degree of reflection of each of the pretreated cloths, black tea-stained cloths, and bleached cloths was measured by using a photoelectric reflection meter (ELREPHO produced by Carl Zeiss Co., Ltd.) and the bleaching ratio thereof was obtained by the following equation (3):

$$\text{Bleaching ratio (\%)} = \frac{(\text{Reflection degree of bleached cloth}) - (\text{reflection degree of black tea-stained cloth})}{(\text{Reflection degree of pretreated cloth}) - (\text{reflection degree of black tea-stained cloth})} \times 100 \quad (3)$$

In this test, when the bleaching ratio increased by 5%, an improvement in whiteness could be seen even by observation with the naked eye, and thus an improvement in the practical bleaching effect could be perceived.

Method of measuring discoloration

(i) Bleaching composition

A bleaching bath the same as that used in the bleaching test was prepared and two pieces of dyed cloth were then added into the bath, followed by bleaching treatment for 30 minutes. The cloths were then washed with water and dried with air, and the lightness and shade thereof were measured by using a differential colorimeter (DICOM ND504DE model produced by Nihon Denshoku-kogyo Co., Ltd.). The degree of discoloration E was determined by the following equation (4):

$$\Delta E = \sqrt{\Delta L^2 + \Delta a^2 + \Delta b^2} \quad (4)$$

wherein ΔL : change in lightness before and after the bleaching of the cloths.

Δa , Δb : change in shade before and after the bleaching of the cloths.

(A larger value of a means a redder color and a smaller value means a greener color. A larger value of b means a yellower color and a smaller value means a bluer color.)

In this test, when the degree of discoloration ΔE was 10 or more, the occurrence of discoloration could be noticed even by observation with the naked eye and thus a large discoloration was actually perceived.

(ii) Bleaching-detergent composition

A piece of dyed cloth was fixed at the four corners in a frame by using pins. 0.5 g of each of the bleaching-detergent compositions of Examples and Comparative Examples was sprinkled over this cloth, and water was then sprayed thereon. After being allowed to stand for 15 minutes, the cloth was washed with water and then dried with air. After drying, the state of the cloth was evaluated on the basis of the criteria described below for the purpose of measuring the degree of discoloration.

3 marks: The parts in contact with each bleaching-detergent composition were remarkably discolored and many spots were observed.

2 marks: The parts in contact with each bleaching-detergent composition were discolored and spots were clearly observed.

1 marks: The parts in contact with each bleaching-detergent composition were slightly discolored and few spots were observed.

0 marks: The parts in contact with each bleaching-detergent composition were not discolored at all and no spots were observed.

Example 1

The bleaching and discoloration tests were performed by using hydrogen peroxide or sodium percarbonate as the component (A) in combination with an amine compound and a compound capable of forming a hypohalous acid ion in the solution. The results obtained are summarized in Table 1.

The amounts of the components constituting the composition shown in Table 1 were as follows:

component (A): 0 or 1×10^{-2} mol/l (in terms of H_2O_2)

component (B): 0 or 1×10^{-2} mol/l %

component (C): 0 or 1×10^{-2} mol/l %

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Table 1

		Component (A)	(B)	(C)	Bleaching rate (%)	Discoloration (ΔE)
Comparative Examples	1	Sodium percarbonate	-	-	20	1.0
	2	"	4-Hydroxy-2,2,6,6-tetramethylpiperidine	-	20	1.0
	3	"	-	Chloramine T	31	1.5
	4	-	4-Hydroxy-2,2,6,6-tetramethylpiperidine	"	10	1.0
	5	Sodium percarbonate	n-Butylamine	"	33	1.5
	6	"	Isopropylamine	"	32	1.5
	7	"	-	Na dichloroisocyanurate	15	1.0
	8	-	-	"	42	20.0
	9	Sodium percarbonate	-	N-chlorohippuric acid	45	15.0
	10	"	-	Na hypochlorate	10	2.0
Present invention	11	"	4-Hydroxy-2,2,6,6-tetramethylpiperidine	Chloramine T	49	3.0
	12	"	4-(N,N-Dimethylamino)-2,2,6,6-tetramethylpiperidine	"	49	1.5
	13	"	4-(N-Acetyl-N-methylamino)-2,2,6,6-tetramethylpiperidine	"	50	2.0
	14	"	3-t-Butylamino-1,2-propanediol	"	49	1.5
	15	"	t-Butylamine	"	50	1.5
	16	"	4-Hydroxy-2,2,6,6-tetramethylpiperidine hydrochloride	"	50	1.5
	17	"	4-Methylamino-2,2,6,6-tetramethylpiperidine	"	52	1.5
	18	"	4-Acetoxy-2,2,6,6-tetramethylpiperidine	"	48	1.5
	19	"	8-Aza-2-hydroxy-methyl-7,7,9,9-tetramethyl-1,4-dioxaspiro[4,5]decane	"	46	1.5

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		Component (A)	(B)	(C)	Bleaching rate (%)	Discoloration (ΔE)
10	Present invention	20 Sodium percarbonate	4-[N-(2-hydroxy ethyl)-N-butylamino]-2,2,6,6-tetramethylpiperidine	Chloramine T	45	1.5
		21 "	2-t-butylamino ethanol	"	51	1.5
15		22 "	4-hydroxy-2,2,6,6-tetramethylpiperidine	Na-dichloroisocyanurate	45	4.0
		23 "	"	Na hydrochlorite	44	2.0
20		24 "	"	N-chlorohippuric acid	50	4.5
		25 "	"	Chloramine B	49	3.0
		26 "	"	Halazone	45	1.5
25		27 Hydrogen peroxide	"	Chloramine T	49	3.0

It is apparent from Table 1 that an excellent effect could be obtained by using the combination of the three components according to the present invention (Nos. 11 to 27), while sufficient bleaching power was not exhibited (Nos. 1 to 4) or the degree of discoloration was high (Nos. 8 and 9) when the components (A) to (C) were used singly or a combination of two or them was used.

35 Example 2

Bleaching tests were conducted in the same manner as that of Example 1 except that 1.0×10^{-2} mol/l (in terms of H_2O_2) of sodium percarbonate was used as the component (A) and the ratio of the component (B) (4-hydroxy-2,2,6,6-tetramethylpiperidine) to the component (C) (chloramine T) was varied. The results are shown in Table 2.

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Table 2

No.	Molar ratio		Bleaching rate (%)	Degree of discoloration ΔE
	(A) / (B)	(A) / (C)		
1	90 / 10	50 / 50	40	1.5
2	70 / 30	"	45	2.0
3	50 / 50	"	49	3.0
4	40 / 60	"	49	4.0
5	70 / 30	80 / 20	41	2.0
6	60 / 40	70 / 30	43	2.5
7	60 / 40	50 / 50	48	3.0
8	60 / 40	40 / 60	42	3.0

Example 3

A granular detergent having the composition shown in Table 3 was mixed with sodium perborate monohydrate as the hydrogen peroxide addition compound, chloramine T and/or sodium dichloroisocyanurate as the chlorine-containing compound and 4-hydroxy-2,2,6,6-tetramethylpiperidine and/or t-butylaminoethanol as the amine to give a powdery bleaching detergent composition shown in Table 4. The composition was subjected to the bleaching and discoloration tests.

The sodium perborate monohydrate used had its dissolution velocity delayed by granulation.

Table 3

Component	Content
	(wt%)
LAS-Na*1	10
AS-Na*2	2
AOS-Na*3	10
Zeolite (4A type)	16
Sodium silicate	10
Sodium carbonate	10
Tinopearl CSB-X*4	0.2
Enzyme (alkalase 2.0T)*5	0.4
Water	5
Sodium sulfate	balance

- *1) Sodium linear alkylbenzenesulfonate in which the alkyl
has 12 carbon atoms.
- 5 *2) Sodium alkylsulfate having 10 to 16 carbon atoms.
- *3) Sodium α -olefin sulfonate having 14 to 18 carbon
atoms.
- 10 *4) A distyrylbiphenyl-type fluorescent brightener.
- *5) The enzyme was subjected to powder blending after
15 spraying and drying.

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Table 4

Sample No.	Comp. Ex.			Present invention				Comp. Ex.		
	1	2	3	4	5	6	7	8	9	10
Composition (parts by weight)	Sodium perborate monohydrate									
	5	0	0	5	5	5	5	10	5	
	Granular detergent									
	90	90	90	90	90	90	90	90	90	
	Tetraacetylglycoluril									
	5									
	Sodium dichloroisocyanurate									
Bleaching rate (%)	10					5				
	Bleaching powder									
			10				5			
	Chloramine T									
				5	5					5
	4-Hydroxy-2,2,6,6-tetramethyl-piperidine									
				5		5	5			
Degree of discoloration (marks)	t-Butylamino-1,2-propanediol									
					5					
Bleaching rate (%)										
Degree of discoloration (marks)	48	50	50	50	48	45	45	30	30	
	3	3	3	0	0	1	1	0	0	

It is apparent from Table 4 that a detergent composition capable of attaining the object of the present invention can be obtained by combining the three components (A), (B) and (C) of the present invention owing to this synergistic effect according to the present invention Nos. 4 - 7, though a bleaching detergent composition which exhibits excellent bleaching power at a relatively low temperature without causing discoloration cannot be obtained by adding the peracid precursor as the activating agent (No. 1), by using the active chlorine compound alone (Nos. 2 and 3) or by using H_2O_2 addition product alone or in combination with the active chlorine compound (Nos. 8 and 9).

Example 4

Granular detergents having compositions shown in Tables 5 and 6 were prepared. Sodium perborate monohydrate, 4-hydroxy-2,2,6,6-tetramethylpiperidine as the specified amine and chloramine T as the chlorine-containing compound were added each in an amount of 5% to the compositions to give bleaching detergent compositions, which were then subjected to the bleaching test and discoloration test.

They exhibited excellent bleaching effect and were free from the discoloration, like the composition No. 4 shown in Table 4.

Table 5

Component	Content
	(wt%)
LAS-Na	7.0
Fatty alcohol ethoxylate*1	2.5
Sodium soap*2	2.5
Sodium tripolyphosphate	36
Sodium silicate	6
Ethylenediaminetetraacetate (EDTA)	0.1
Tinoparl CBS-X	0.2
Sodium carboxymethyl cellulose	0.5
Water	8
Sodium sulfate	balance

*1) Fatty alcohol ethoxylate, the alcohol having 16 to 18 carbon atoms and EO \bar{P} of 7.

*2) Sodium salt of fatty acid soap having 16 to 18 carbon atoms.

Table 6

5	Component	Content
		(wt%)
	LAS-Na	12
10	As-Na	5
	AES-Na*1	5
15	Zeolite (4A)	12
	Sodium silicate	15
	Sodium carbonate	3
20	Tinoparl CBS-X	0.2
	Water	5
	Sodium sulfate	balance

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*1) Sodium alkylether sulfate having 12 to 15 carbon atoms and EO \bar{P} of 3.

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Example 5

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Bleaching-detergent compositions were formed in the same manner as that of Example 4 except that sodium percarbonate was used as the hydrogen peroxide addition compound. The compositions were subjected to the bleaching and discoloration tests to obtain the results similar to those of Example 4.

Claims

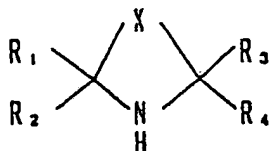
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1. A bleaching composition comprising:
 - (A) hydrogen peroxide and/or a hydrogen peroxide addition compound;
 - (B) a hindered amine compound selected from the group consisting of heterocyclic hindered amines, acyclic hindered amine compounds and salts thereof; and
 - (C) an active halogen-containing compound capable of forming a hypohalogenous acid ion in an aqueous solution.

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2. A composition according to Claim 1, wherein the component (B) is a heterocyclic hindered amine compound having the following General Formula [I] or a salt thereof:

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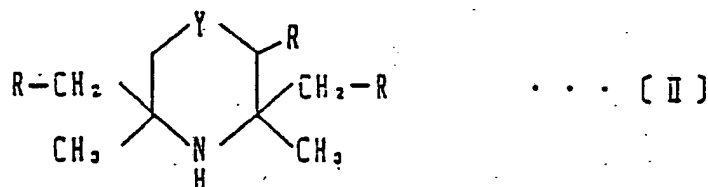


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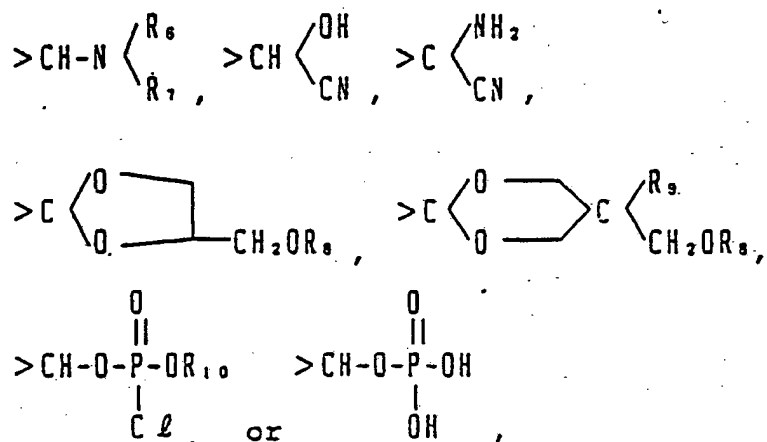
(wherein R₁ to R₄ each donates a lower alkyl group and may be the same as or different from each other,

or R₁ and R₂ or R₃ and R₄ may bonded to each other to form a 5-membered or 6-membered alicyclic ring involving the carbon atoms to which they are bonded, and X donates a divalent organic residue).

3. A composition according to Claim 1, wherein the component (B) is a heterocyclic hindered amine compound having the following General Formula [II] or a salt thereof:

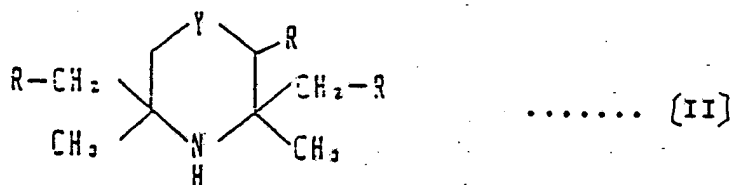


wherein R donates hydrogen or methyl group and Y donates $>CH_2$, $>C=O$, $>CH-OR_5$,

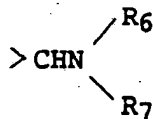


in which R₅, R₆, R₇ and R₈ may be the same or different and each donates a hydrogen atom, a lower alkyl group, C_mH_{2m}OH, C_mH_{2m-1}(OH)₂, C_mH_{2m}COOM₁, m being an integer from 1 to 4 and M₁ being a hydrogen atom or an alkali metal, an aliphatic, aromatic or araliphatic acyl group or a substituted or unsubstituted carbamoyl group; R₉ donates a methyl group or an ethyl group; and R₁₀ donates a lower alkyl group or an aryl group.

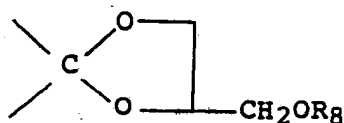
4. A composition according to Claim 1, wherein the component (B) is a heterocyclic hindered amine compound having the following General Formula [II] or a salt thereof:



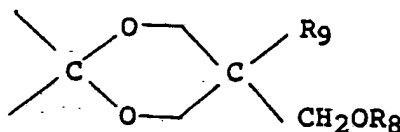
wherein R is hydrogen or methyl, Y is $>CH_2$, $>CH-OR_5$ (in which R_5 is hydrogen or lower alkyl),



(in which both of R₆ and R₇ are hydrogen, or R₆ is hydrogen or lower alkyl and R₇ is lower alkyl, lower aliphatic acyl, carbamoyl, mono- or di-lower alkyl carbamoyl, or lower hydroxy alkyl),

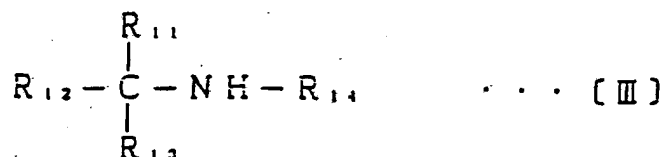


(in which R_8 is hydrogen, lower alkyl, lower aliphatic acyl, carbamoyl, or mono- or di-lower alkyl carbamoyl)
or



(in which R_8 is as defined above and R_9 is methyl or ethyl).

5. A composition according to Claim 1, wherein the component (B) is an acyclic hindered amine compound having the following General Formula [III] or a salt thereof:



wherein R_{11} , R_{12} and R_{13} each donate

$-\text{COOH}$, $-\text{C}_n\text{H}_{2n-1}$, $-\text{C} \nmid \text{C}_n\text{H}_{2n-1}$,³

$-\text{C}_n\text{H}_{2n}\text{OH}$, $-\text{CH}_2-\text{C} \nmid \text{C}_n\text{H}_{2n-1}$,³

$-\text{C}_n\text{H}_{2n}\text{COOH}$, $-\text{OC}_n\text{H}_{2n+1}$ or

$-\text{COOR}_{15}$, (in which R_{15} being an alkyl group having 1 to 9 carbon atoms and n is an integer of 1 to 9) and

R_{14} donates $-\text{H}$, $-\text{C}_n\text{H}_{2n-1}$,

$-\text{C} \nmid \text{C}_n\text{H}_{2n-1}$,³, $-\text{C}_n\text{H}_{2n}\text{OH}$,

$-\text{CH}_2-\text{C} \nmid \text{C}_n\text{H}_{2n-1}$,³

$-\text{C}_n\text{H}_{2n-1}(\text{OH})_2$, $-(\text{C}_2\text{H}_4\text{O})_n\text{H}$,

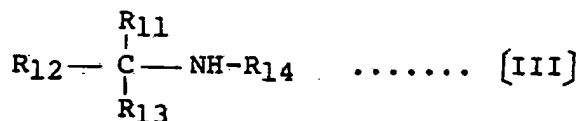
$-\text{C}_n\text{H}_{2n}\text{COOH}$, $-\text{C}_n\text{H}_{2n}\text{COOR}_{15}$,

$-\text{C}_n\text{H}_{2n}\text{SO}_3\text{M}_2$, $-\text{C}_n\text{H}_{2n}\text{OSO}_3\text{M}_2$,

$-\text{C}_n\text{H}_{2n}\text{PO}_3\text{H}$ or $-\text{C}_n\text{H}_{2n}\text{CN}$,

in which R_{15} is an alkyl group having 1 to 9 carbon atoms, n is an integer of 1 to 9 and M_2 is H or an alkali metal.

6. A composition according to Claim 1, wherein the compound (B) is an acyclic hindered amine compound having the following General Formula [III] or salt thereof:



wherein each of R_{11} , R_{12} and R_{13} is $-\text{C}_n\text{H}_{2n-1}$ or $-\text{C}_n\text{H}_{2n}\text{OH}$ (in which n is 1 - 4) and R_{14} is H, $-\text{C}_n\text{H}_{2n-1}$, $-\text{C}_n\text{H}_{2n}\text{OH}$, $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{OH}$ or $-\text{C}_n\text{H}_{2n-1}\text{SO}_3\text{M}_2$ (in which n is 1 - 4 and M_2 is H or Alkali metal).

7. A composition according to Claim 1 which contains 0.05 to 4 mol of the component (C) and 0.05 to 4 mol of the component (B) per mol of hydrogen peroxide formed from the component (A).

8. A composition according to claim 1, wherein the hydrogen peroxide addition compound is selected from the group consisting of percarbonates, perborate, perphosphoric acid and salts thereof.

9. A composition according to claim 1, wherein the active halogen-containing compound of component (C) is selected from the group consisting of sodium N-chloro-p-toluenesulfonamide, sodium N-chlorobenzenesulfonamide, N-chlorosulfonamide, sodium N-cyclohexyl-N-chlorosulfonamide, N,N-dichlorosulfamoylbenzoic acid, N,N-dichloro-p-toluenesulfonamide, N,N-dichlorobenzenesulfonamide, N-chlorosaccharin, N-

chloromethanesulfonamide, N-chlorosulfamic acid, N-bromoacetamide, N-chlorosuccinimide, N-chlorohippurates, N-chloro-N-methylglycine, N-chloro-N-ethyl-o-carbobenzamide, N-chloro-ethylcarbamate, N-chloroacetanilide, N-chloro-o-carbobenzamide, N-chloro-N-methyl-o-carbobenzamide, chlorinated acetone/urea condensate, hypochlorites, and mono-di- and trichloroisocyanuric acids.

5 10. A composition according to claim 9, wherein the active halogen-containing compound is selected from the group consisting of N-halosulfonamides, N-haloamides, hypohalogenous acid salts and halogenated isocyanurates.

11. A bleaching detergent composition comprising:

(A) 0.1 to 30 wt.% of hydrogen peroxide and/or a halogen peroxide addition compound:

10 (B) 0.1 to 30 wt.% of a hindered amine compound selected from the group consisting of heterocyclic hindered amines, acyclic hindered amine compounds and salts thereof; and

(c) 0.1 to 30 wt.% of an active halogen-containing compound capable of forming a hypohalogenous acid ion in an aqueous solution.

15 12. A bleaching detergent composition according to claim 11, wherein the composition further contains at least one surfactant in an amount of 0.1 to 50% by weight.

13. A bleaching detergent composition according to claim 11, wherein the composition further contains at least one builder in an amount of 5 to 90% by weight.

20 14. A bleaching detergent composition according to claim 11, wherein the composition further contains an enzyme in an amount of 0.01 to 10% by weight.

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